A STUDY OF THE PYROLYTIC AND PHOTOLYTIC DECOMPOSITION OF TRITYL PIVALATE AND TRITYL P-TOLUATE

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CHAPTER I

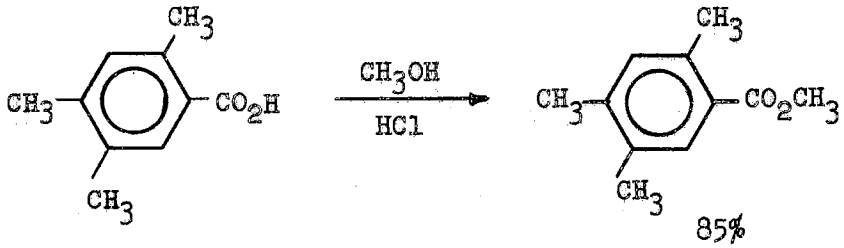
INTRODUCTION

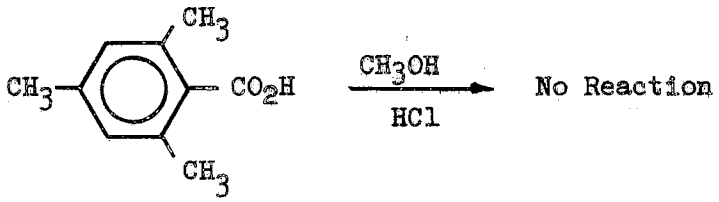
Although trityl esters have been known for sixty years, relatively few have been prepared. Thermal decomposition of the esters had not been investigated extensively until recently. It was therefore of interest to originate a systematic study of the synthesis and pyrolysis of several trityl esters of aliphatic and aromatic acids in an effort to gain insight as to the fate of acyloxy, aryloxy and trityl radicals at high temperature.

CHAPTER II

HISTORICAL

The synthesis of hindered esters has often been a difficult problem. A discussion of the synthesis of the methyl esters of ortho-substituted benzoic acids by Wheland (39) via the combined action of methanol and hydrogen chloride illustrates the increasing difficulty of esterification as the number and size of groups increase at the ortho-positions. Whereas, with 2,4,5-trimethylbenzoic acid an 85 per cent yield of the methyl ester was obtained, no ester was produced from 2,4,6-trimethylbenzoic acid or 2,6-dinitrobenzoic acid. However, mesitylacetic acid is readily esterified which illustrates a proximity effect when the carbonyl group is removed from the ring by one carbon atom. In contrast, the silver salts of the hindered acids were esterified readily with methyl iodide.





Initially it was suggested that the silver atom was responsible for the resulting esterification by holding the blocking substituents away from the carbonyl function. A more plausible explanation is that the reaction occurs at the carboxyl oxygen atom. With an alcohol and hydrogen chloride the reaction is believed to take place at the carboxyl carbon atom. The mechanism suggested for the reaction involving the silver salt of the acid and the alkyl halide should be affected less by ortho-substituents on the benzene ring since the reaction site is two atoms further from the ring. It seems reasonable to postulate attack at the carbonyl oxygen atom in a nucleophilic displacement step.

In another preparation of the methyl ester of a hindered acid, a solution of 2,4,6-trimethylbenzoic acid dissolved in 100 per cent sulfuric acid, was poured into cold methanol. That benzoic acid was not esterified when treated in the same manner indicated a different mechanism was most likely operative in which steric effects were not important.

Only a few esters of the highly hindered alcohol, triphenylcarbinol, have been synthesized. The first attempt was reported by Gomberg and Davis in 1903 (22). Triphenylmethyl acetate [trityl acetate (I)] was prepared by several methods; the best yield was obtained by heating trityl chloride with an excess of silver acetate under reflux in benzene for three hours.

$$CH_3CO_2Ag + (C_6H_5)_3C\,Cl \longrightarrow CH_3CO_2C(C_6H_5)_3 + AgCl$$

I

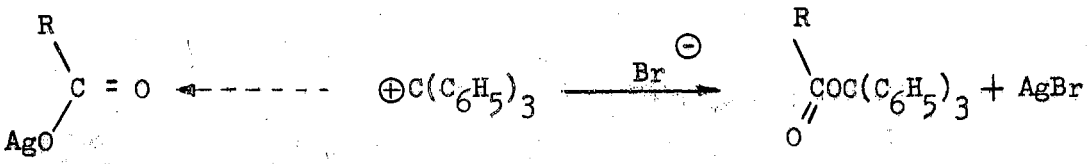
Schoepfle (34) prepared I (95 per cent) by shaking a solution of trityl bromide in benzene with ammonium acetate for ten hours. Trityl benzoate and trityl p-phenylbenzoate were isolated by Wieland in 1937 (42) as products from the reaction of trityl radical with the corresponding acid

peroxide. Wieland and Meyer (41) reported in 1942 the preparation of trityl p-toluate (II) from trityl radical and di-p-toluoyl peroxide and also via the silver salt method mentioned previously (22). Trityl p-anisate was also prepared by both methods.

$$(C_6H_5)_3C\cdot + (p\text{-}CH_3C_6H_4CO_2)_2 \longrightarrow \underset{\text{II}}{p\text{-}CH_3C_6H_4CO_2C(C_6H_5)_3} + p\text{-}CH_3C_6H_4CO_2\cdot$$

Bowden and Watkins (11) have reported the synthesis of trityl formate by dissolving triphenylcarbinol in anhydrous formic acid. However, the compound is unstable above 49° and decomposes spontaneously to give triphenylmethane and carbon dioxide. In 1950 Hammond and Rudesill (23) recorded the preparation of trityl benzoate in 40 per cent yield by the reaction of sodium benzoate with trityl chloride at reflux in acetone. In general, the yields of trityl esters were quite low or unspecified in the early work. Recently, Berlin and co-workers (10) prepared several new trityl esters in high yields (60 to 94 per cent) by heating a solution of trityl bromide in dry benzene or cyclohexane with a slight excess of the salt of the acid (sodium, potassium, and silver salts). The solutions were stirred and heated at reflux for periods ranging from two to six hours. Improved yields of previously prepared esters were also noted. Two possible mechanisms for the reaction were proposed. Postulated ionization of trityl bromide in benzene (14) suggested that a parallel, classical carbonium ion esterification, via attack by the trityl ion on either the carboxylate anion or the salt, might be operative. More attractive, however, is the seemingly close relationship to the esterification of the silver salt of 2,4,6-trimethylbenzoic acid with methyl iodide (37). In this latter reaction the mechanism probably involves a displacement on

the alkyl halide by the carbonyl oxygen of the salt. Trityl carbonium ion is feasible in the former case and could attack the carbonyl oxygen atom.



Only a few experiments involving the pyrolysis of carbonyl compounds containing a trityl group have been reported. Fuson and Berlin (19) investigated the thermal decomposition of three trityl ketones resulting from the 1,4-addition of the Grignard reagents of phenyl, p-tolyl, and o-tolyl bromides to 1-naphthyl trityl ketone. Pyrolysis of the compounds at temperatures ranging from 230° to 245° gave triphenylmethane, carbon monoxide, and the corresponding 2-substituted naphthalenes in high yields. For example, 1-(1,2-dihydro-2-p-tolyl) naphthyl trityl ketone gave triphenylmethane in 90 per cent yield and 2-p-tolylnaphthalene in 85 per cent yield. A qualitative test indicated the production of carbon monoxide.

Triphenylacetaldehyde has been reported to give triphenylmethane and carbon monoxide upon heating (31). Similarly, when β-benzopinacolone was distilled below 465°, triphenylmethane was the main product with smaller amounts of p-benzoyltriphenylmethane, benzene, and benzophenone (13).

The pyrolysis of trityl triphenylacetate and di-trityl fumarate appear to be the first reported pyrolysis of trityl esters (3). In both cases, triphenylmethane and carbon dioxide were the only products identified. In 1913 Gomberg (21) pointed out that the di-trityl ester of carbonic acid, upon heating at reflux in xylene in the presence of finely-

divided copper gave carbon dioxide and di-trityl ether as the major products. As mentioned previously (11) trityl formate, although stable at room temperature, decomposed near 49° to give triphenylmethane and carbon dioxide. Jones and Ritchie (26) have recently reported the pyrolysis of trityl benzoate (IV) at 225° and 500°. The main products obtained at the higher temperature were benzoic acid, triphenylmethane, tetraphenylmethane, and carbon dioxide. Benzene, carbon monoxide and benzoic anhydride were produced in small quantities. At 225° only benzoic acid and triphenylmethane were identified although an unknown compound was isolated. In both cases much tar was formed. Actually, the yield of tetraphenylmethane recorded suggests the method is of preparative value.

$$\underset{\text{IV}}{C_6H_5CO_2C(C_6H_5)_3} \xrightarrow{500^\circ} (C_6H_5)_4C + (C_6H_5)_3CH + C_6H_5CO_2H + CO_2$$

Berlin and co-workers have pyrolyzed several trityl esters (9). Decomposition of trityl propionate at temperatures over the range 220° to 310° gave reproducable results with the major products identified in high yield as propionic acid and triphenylmethane. Appreciable quantities of carbon dioxide, benzophenone, and a copolymer were obtained along with several other compounds present in small amounts. Pyrolysis of trityl hydrocinnamate similarly gave high yields of triphenylmethane and a mixture of hydrocinnamic acid and anhydride. Carbon dioxide, styrene, and benzophenone were formed in addition to a few minor products. In general homolytic fission to generate acyloxy and trityl radicals occurred. In view of the instability of acyloxy radicals (15) and the large recovery of aliphatic acids, rapid abstraction of hydrogen by acyloxy radicals was postulated (9).

Pyrolysis of acetates and xanthates has long been a preferred method

for the preparation of olefins (16). The reaction is believed to proceed via the concerted mechanism as illustrated below with cyclohexyl acetate. An extensive

study of the effect of molecular size and structure on the pyrolysis of several esters of cyclohexanol was reported in 1957 by Smith and Wetzel (35). The pyrolyses followed the classical pattern with production of cyclohexene and the corresponding acid. Of particular interest to our work was the pyrolysis of cyclohexyl benzoate and cyclohexyl p-toluate. The temperatures required for maximum yield of the corresponding acids were 465° and 464°, respectively (yields 98.2 per cent and 98.7 per cent). Rashbrook and Taylor (32) have reported recently the pyrolysis of vinyl benzoate and vinyl p-toluate at various temperatures. Thermal polymerization of vinyl benzoate appeared to occur below 350° when the ester was heated in an evacuated pyrex tube. Above 350° benzoic acid and a highly colored tar were the main products although carbon dioxide and traces of carbon monoxide, acetaldehyde, benzoic anhydride, and low molecular weight hydrocarbons were detected. At 450° in a flow-reactor acetophenone (40 per cent), styrene (20 per cent), biphenyl (20 per cent), benzene and trace components were produced. Pyrolysis of vinyl p-toluate was reported to follow the same pattern.

In 1929 Conant and co-workers (12) reported that the photochemical decay of trimethylacetaldehyde gave isobutane and carbon monoxide. Thus if the t-butyl radical was formed in our work it would be expected to decay to give some isobutane.

Recently, Zimmerman and Somasekhara (43) have reported the photochemical hydrolysis of several substituted-phenyl trityl ethers. In all cases except p-nitrophenyl trityl ether, 9-phenylfluorene was produced along with the substituted phenol and triphenylcarbinol. Photolysis of m-nitrophenyl trityl ether in water gave m-nitrophenol in 81 per cent yield, triphenylcarbinol in 65 per cent yield and 9-phenylfluorene in 20 per cent yield. Although an ionic mechanism is postulated in the formal part of the paper, a footnote contains reference to trityl peroxide and a radical mechanism is a suggested possibility.

CHAPTER III

DISCUSSION OF RESULTS AND CONCLUSIONS

It was the object of this research to develop a general synthetic procedure for trityl esters and to study the behavior of such compounds under pyrolysis conditions. Moreover, it was hopefully anticipated that homolytic bond fission might occur via pyrolysis and/or photolysis of the esters to produce trityl and acyloxy radicals. Consequently, an investigation of the fate of acyloxy and aroyloxy radicals under these conditions was considered an attractive realm in which to expand. In view of the work of Jones and Ritchie concerning the isolation of tetraphenylmethane from thermal decomposition of trityl benzoate (25), the pyrolysis study of several trityl esters might provide a convenient method for synthesis of 1, 1, 1-triarylmethyl-substituted hydrocarbons.

In the preparation of the two esters, trityl pivalate (III) and trityl p-toluate (II), best results were obtained when the corresponding sodium salt of the acid was allowed to react with trityl bromide in refluxing benzene.

$$RCO_2Na + (C_6H_5)_3C\ Br \longrightarrow RCO_2C(C_6H_5)_3 + NaBr$$

II. R = $\underline{p}$-$CH_3C_6H_4$ -

III. R = $(CH_3)_3C$-

During the reaction, the light yellow benzene solution gradually became a deep yellow color. Simultaneously, the solid material changed from a fairly coarse texture to a finely-divided, white solid, indicative of

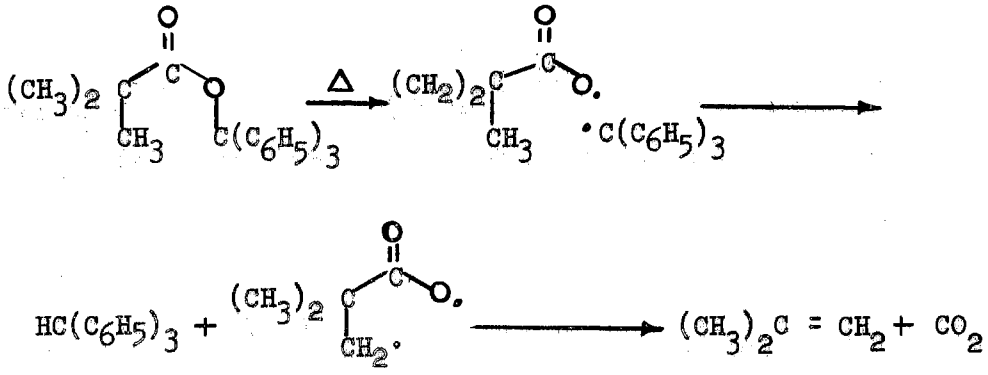
sodium bromide. When potassium pivalate was substituted for the sodium salt, lower yields of pure ester (III) were obtained. The benzene solution, after filtration to remove the inorganic salt, formed a gel upon concentration. It was thought that this gel was excess potassium pivalate, apparently soluble in benzene to some extent. Recrystallization of the ester presented some difficulties because of its high solubility in most common solvents. Cyclohexane and n-heptane were employed with some success but Skelly Solvent F afforded the best results. Trityl p-toluate (II) could be recrystallized from benzene or methyl ethyl ketone, although the latter solvent was preferred.

As mentioned previously (10), the reaction mechanism proposed included a nucleophilic attack on trityl bromide by the carbonyl oxygen atom of the salt or carboxylate anion. A reasonable alternative is the electrophilic attack by trityl carbonium ion on the carbonyl oxygen atom of the salt or its anion since the ionization of trityl bromide in benzene solution has been postulated (14). In summary, the reaction of trityl bromide with acid salts in hydrocarbon solvents is an efficient synthetic route to trityl esters. In preliminary experiments, trityl chloride proved to be quite reactive but its hygroscopic nature created a tedious recrystallization procedure with concomitant lower yields of esters.

The thermal decomposition of trityl pivalate (III) appeared to occur in a very specific manner as carbon dioxide, isobutylene and triphenylmethane were obtained in nearly equal and very high yields. The presence of small amounts of biphenyl, benzophenone and triphenylcarbinol indicated that a minor decomposition resulting from acyl-oxygen bond fission was also operative. Attempted pyrolysis in a static system

after three hours at 300° resulted in the recovery of mostly unreacted ester. Only a small amount of decomposition occurred at 350° in a rapid flow pyrolysis system, but at 425° nearly complete decomposition was observed.

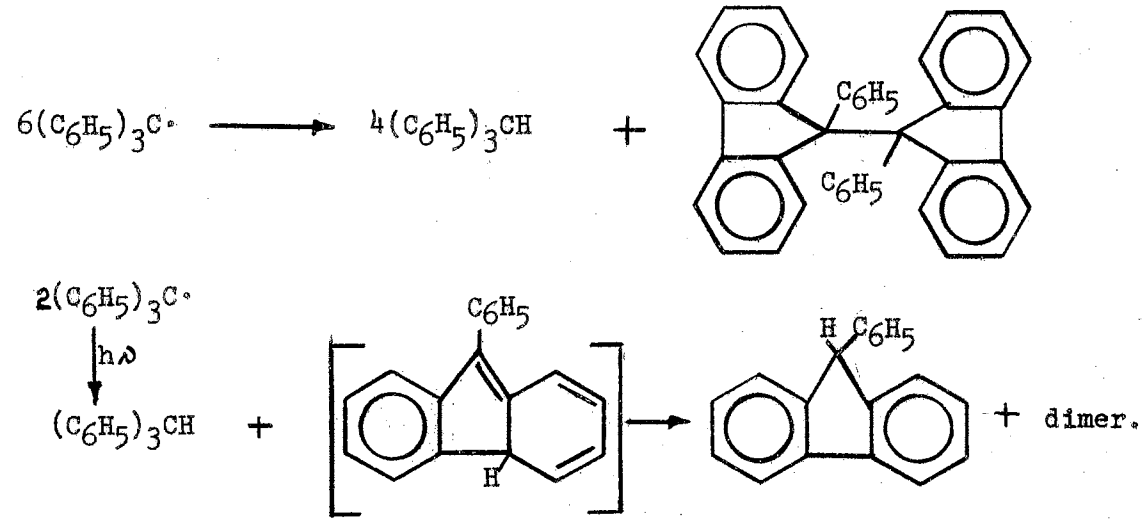
The major route of pyrolysis appeared to be alkyl-oxygen bond fission producing trityl radical and pivaloyloxy radical. Since pivalic acid is known to be stable at 450° (5), it was probably not formed during the pyrolysis. This suggests that the initial bond cleavage is followed by immediate abstraction of hydrogen by trityl radical from the pivaloyloxy radical followed by collapse of the product to form isobutylene and carbon dioxide. As no isobutane was detected, formation of t-butyl radical likely did not occur, as it would be expected to abstract hydrogen forming isobutane in a disproportionation step (12).



The trityl group appears to be in close proximity to a methyl hydrogen atom in a molecular model of the ester III using Courtauld models and a concerted mechanism could indeed be speculated. However, results obtained from the pyrolyses of trityl propionate and trityl hydrocinnamate (9) indicate that trityl radical was formed readily suggesting that a completely concerted

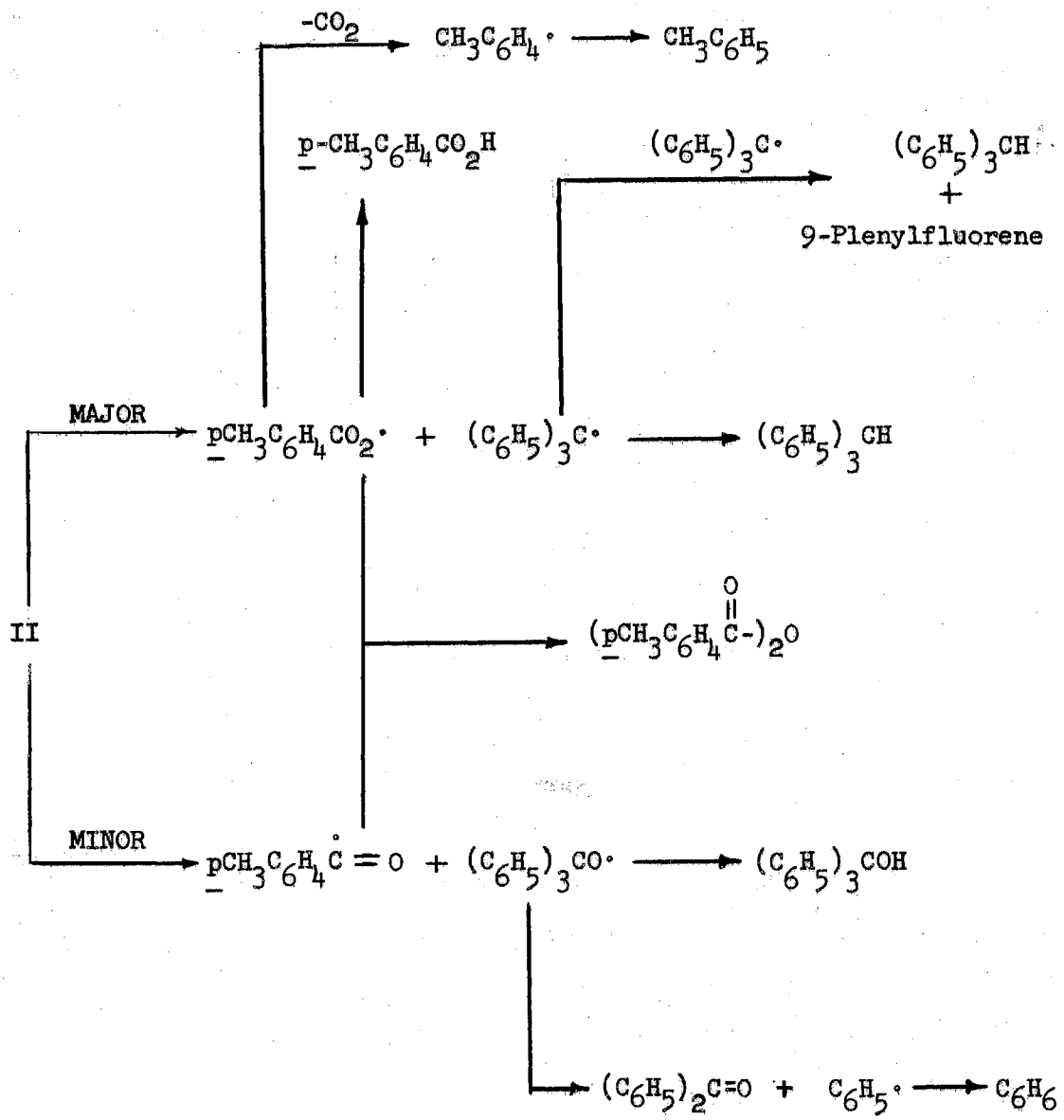
mechanism is unlikely. Nevertheless, the high yields of products obtained strongly supports a mechanism (such as discussed above) which may involve radical pairs or a cage effect.

Trityl p-toluate (II) was found to decompose at 340° in a rapid flow system. At 375° decomposition was incomplete as more than 25 per cent of the ester was recovered. Incomplete decomposition was also observed in the static system at 250° after six hours. Major cleavage occurred at the alkyl-oxygen bond as triphenylmethane and p-toluic acid were the main products formed. The detection of 9-phenylfluorene in the pyrolysate of II is further evidence for homolytic alkyl-oxygen bond cleavage as it has been reported that trityl radicals disproportionate in the presence of light to triphenylmethane and the dimer of 9-phenylfluorene (33). Irradiation of trityl radical has been shown to produce both 9-phenylfluorene and its dimer (28).

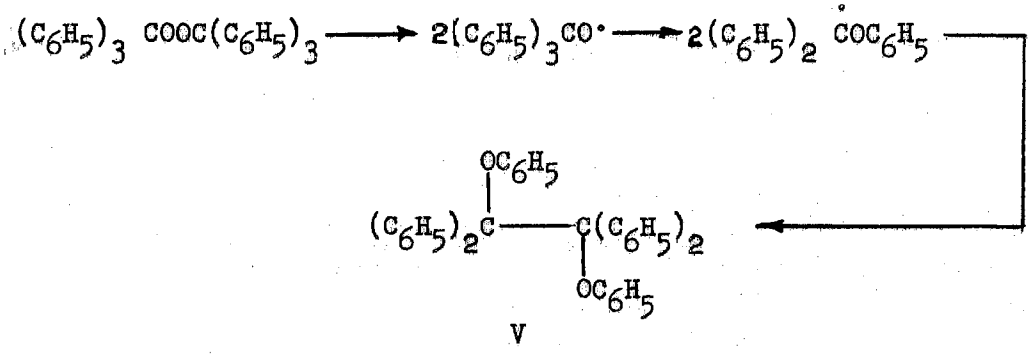


The presence of carbon dioxide and toluene in the pyrolysates of II indicate a minor decarboxylation route probably via the decomposition of the p-toluoyloxy radical formed initially. Other workers have obtained similar results (i.e. isolation of large amounts of acid and small

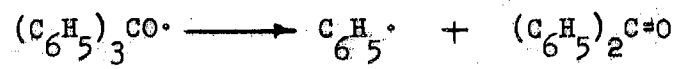
amounts of carbon dioxide) in the pyrolyses of benzoate and p-toluate esters (32, 26, 35). Another parallelism is the production of the anhydride of p-toluic acid observed in pyrolysis of III in the static system. The flow chart below shows most of the products detected in the pyrolysate of II and the suggested routes of formation.



Hurd (25) had earlier predicted that trityl benzoate (IV) should decompose in a reaction involving disproportionation of radicals to yield benzoic anhydride and di-trityl ether. Jones and Ritchie (26) found small amounts of benzoic anhydride in the pyrolysate of IV but did not isolate any di-trityl ether which had been reported to decompose at its melting point (21). Trityl peroxide, which could be formed by the coupling of two triphenylmethoxy radicals, was identified in the pyrolysate of II in our work. However, whether it was formed via the coupling reaction or by oxidation of hexaphenylethane is problematical (20). Hexaphenylethane could clearly be a conceivable product from the pyrolysis of II via the coupling of two trityl radicals (20). It is felt that the latter explanation is more correct as trityl peroxide is known to be unstable upon heating in solution (20). A discussion of the thermal decomposition of peroxides by Walling seems to be pertinent (37). Trityl peroxide decomposes to form triphenylmethoxy radicals which, after rearrangement, couple to form the di-ether V. The decomposition follows another path also since biphenyl and benzophenone were identified (40).



V

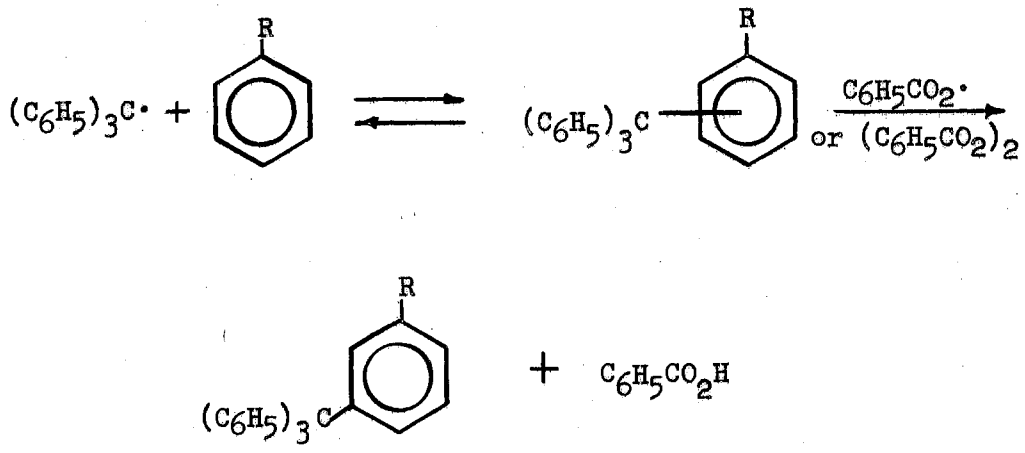


The presence of benzophenone, benzene and biphenyl in our

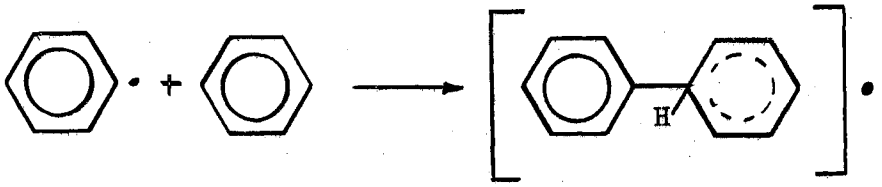
pyrolysates and the inability to isolate any of the di-ether V suggest that at these higher temperatures, the triphenylmethoxy radical decomposes by the route analogous to the decomposition of t-butoxy radicals which forms acetone and methyl radicals (37).

Trityl radicals have been shown to induce the decomposition of several diacyl peroxides (15). In the presence of the more stable acyloxy radicals, namely benzoyloxy and cyclopropylcarboxy radicals, tritylation of benzene occurred forming tetraphenylmethane. However, tetraphenylmethane was not isolated in the decomposition of the peroxides which formed less stable acyloxy radicals. Also, it was noted that the various alkyl radicals derived from decomposition of the less stable acyloxy radicals did not promote the formation of tetraphenylmethane. Benkeser and Schroeder (8) have found that trityl radical reacts with several substituted-benzene solvents in the presence of benzoyl peroxide forming various ratios of ortho-, meta- and para-substituted tetraphenylmethanes. However, in the presence of nitrobenzene no substituted tetraphenylmethanes were isolated. Competitive experiments using mixed solvents showed that the relative reactivity was influenced largely by the nature of the substituent on the benzene ring. Electron withdrawing groups such as triflouromethyl and nitro showed low reactivities relative to benzene while anisole and chlorobenzene showed higher reactivities. Benkeser, therefore, suggested a reaction mechanism involving an intermediate complex between trityl radical and the aromatic solvent. Reaction of this intermediate with benzoyloxy radical or benzoyl peroxide would then form the substituted tetraphenylmethane and benzoic acid. Electron deficient rings such as in nitrobenzene would not be expected to form a strong complex with trityl radical. In our work attack of trityl radical on benzene or coupling

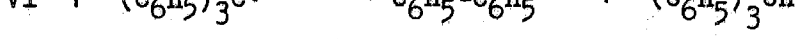
with phenyl radical to form tetraphenylmethane was not observed in the rapid-flow pyrolysis. Similarly p-tolyltriphenylmethane was not detected in the static pyrolysis of trityl p-toluate. This is considered supporting evidence for rapid decay of the aroyloxy and trityl radicals formed.

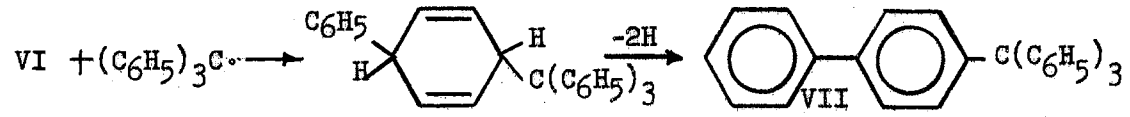


The reaction of phenylazotriphenylmethane with benzene illustrates both hydrogen abstraction and tritylation by the trityl radical (24). Triphenylmethane and biphenyl are formed by abstraction of hydrogen by trityl radical from a proposed radical intermediate VI. Tritylation of biphenyl was also observed with the formation of 4-tritylbiphenyl (VII).



VI





A similar reaction occurred with several other arylazotriarylmethanes. It is therefore not surprising in our work at high temperatures that trityl radical should remove hydrogen in a very fast reaction to form triphenylmethane.

In the photolysis of trityl p-toluate (II) in an oxygen atmosphere, the increased yield of benzophenone suggests rapid oxidation of trityl radical to triphenylmethoxy radical which decomposes to give benzophenone and phenyl radical. This fact in addition to the other identified products which were also found in the pyrolysate, supports a radical mechanism for the decomposition. The negligible decomposition of triphenylmethane when photolyzed in boiling benzene with an inlet oxygen stream virtually eliminates the possibility of formation of triphenylmethoxy radical from triphenylmethane formed in the photolysis of trityl p-toluate. This does not, however, rule out the possible oxidation of triphenylmethane at the high temperature employed for the static pyrolysis of II. The increased yield of triphenylmethoxy radicals at high temperatures also could be explained by the mechanism suggested for the autoxidation of hexaarylethanes whereby the peroxide is formed (38).

$$(C_6H_5)_3C\cdot + O_2 \longrightarrow (C_6H_5)_3COO\cdot \xrightarrow{(C_6H_5)_3C\text{-}C(C_6H_5)_3} \begin{matrix}(C_6H_5)_3C\cdot \\ + \\ [(C_6H_5)_3CO]_2\end{matrix}$$

The trityl peroxide produced by autoxidation of trityl radical would be expected to decompose as discussed previously to form benzophenone and

biphenyl. Triphenylcarbinol and benzene were also found in increased yields in the oxidative static pyrolysis of II. Moreover, the quantity of triphenylcarbinol rose in the photolysis of II in the presence of oxygen. These two products could arise by abstraction of hydrogen by appropriate radical intermediates. The presence of phenol in the static pyrolysis with oxygen might also be explained by the autoxidation of phenyl radical (8).

Unknown 1 in all the pyrolysis and photolysis experiments exhibited the same retention time on two columns by gas chromatography (10 per cent silicone rubber and 20 per cent Apiezon L). As the compound was formed in low yields and none was isolated in pure form, a suggestion as to its identity is based only on retention time related to the retention times of known compounds. From this limited data unknown 1 is speculated to be either 4-methylbiphenyl or 4, 4'-dimethylbiphenyl. Neither of these compounds were readily available and due to the small yields of this unknown obtained, no effort was made to purchase or prepare these compounds for comparison. Unknowns 2 and 3 were present in only trace amounts. Unknown 2, having a retention time identical to diphenylmethane, was tentatively assigned to this structure. However, we were unable to obtain it sufficiently pure for infrared analysis as it always occurred in the presence of large quantities of triphenylmethane, the mixture being inseparable by chromatography on alumina. Unknown 3 (present only in the static pyrolysis of II in the presence of oxygen) was isolated in the presence of a larger amount of benzophenone. The infrared spectrum of the unknown 3 shows a carbonyl band near 1740 $cm.^{-1}$ whereas the carbonyl band for benzophenone occurs at 1660 $cm.^{-1}$ The unknown 3, while not apparent in the chromatogram of the original

pyrolysate, had a retention time very near to that of benzil. The carbonyl of benzil occurs at about 1650 cm.$^{-1}$ however. Therefore, it would appear unlikely that it would be a para-substituted benzil.

The material in fractions 2, 3 and 4 in the static pyrolyses of II (comprising about 10 per cent by weight of the pyrolysate in each case) appeared to be a mixture of an acidic nature. The ultraviolet spectra of these fractions were almost identical and each showed a peak very near one reported in the spectrum of p-toluic acid (29). Infrared analysis of the fractions from both pyrolyses indicated the presence of anhydride. The fractions were soluble in 0.4 N sodium hydroxide solution. After precipitation with concentrated hydrochloric acid, infrared analysis showed that the anhydride carbonyl peaks had disappeared. The spectra of the fractions from the two pyrolyses were almost identical and were similar to the spectrum of p-toluic acid. The material was almost completely soluble in sodium bicarbonate solution, liberating carbon dioxide in each case. Nuclear magnetic resonance studies of fractions 2 and 3 from the static pyrolysis under helium, in acetone solution showed peaks at 3.85, 6.88, and 7.55 delta in a ratio of 3:2:1, respectively. Considerable aliphatic hydrogen (probably methyl hydrogens) are present. A spectrum of the same material in dilute (about 0.4 N) sodium hydroxide solution was compared to that of a similar solution of p-toluic acid and was found to be markedly different.

It was not possible to account entirely for the balance of hydrogen atoms in the identified products. To explain this deficiency, we are forced to assume that the char contains some organic material. With the rapid flow system the charred substance remained on the column and was not soluble in common organic solvents. It was removed with chromic acid

cleaning solution and soap and water. In the static pyrolyses most of the dark brown charred material was soluble in acetone and somewhat soluble in ether. However, these solutions upon standing deposited a dark tarry film on the glass containers.

In summary, a new improved procedure has been developed for the synthesis of trityl esters in good yield. The use of trityl bromide with a variety of acid salts greatly facilitates the purification process.

The pyrolysis of trityl pivalate has been found to occur in a clean manner to form triphenylmethane, isobutylene and carbon dioxide in high yields. The mechanism of decomposition, although undetermined, is believed to be radical rather than ionic in nature and not completely concerted since some charring was noted in the pyrolysis chamber. The degree of charring also affected the final yields of products. Pyrolysis and photolysis of trityl p-toluate were complex and afforded many compounds. Of significance were the high returns of triphenylmethane and p-toluic acid. On the basis of the oxidation experiments with the pyrolysate and the photolysate, a radical mechanism is thought to be operative. In this respect the p-toluoyloxy radical probably abstracts hydrogen rapidly since aroyl peroxides are known to decompose readily at low temperatures. Hydrogen in the melt is primarily of the aromatic-type although the lone methyl group is available. Clearly in view of the high yields of acid and triphenylmethane, the radical precursors must remove hydrogen from one or more common sources perhaps to form biradicals.

To be sure trityl radical is not sufficiently free in the rapid flow pyrolysis to attack benzene to give the expected tetraphenylmethane.

Neither is decarboxylation and subsequent formation of p-methylphenyltriphenylmethane of significance. Within the realm of possibility is the formation of a π-complex between trityl radical and the acyloxy (or aroyloxy) radical prior to the hydrogen abstraction step. This has been suggested to explain reaction of trityl radical with aroyloxy radicals at room temperature (8).

CHAPTER IV

EXPERIMENTAL[1, 2, 3, 4, 5, 6]

Preparation of Sodium Pivalate. A 20 per cent solution by weight of sodium hydroxide (100 g. in 400 ml. of distilled water) was prepared. A sample of pivalic acid (16.16 g.; 0.158 moles) was dissolved in 150 ml. of distilled water. The acid solution was then titrated with the sodium hydroxide solution using a Beckman Model 72 pH meter. A titration curve was plotted (ml. NaOH vs. pH) and the equivalence point was found to be at a pH of approximately 9. Additional acid (8.08 g.; 0.079 moles) was added and the solution was titrated with the base to a pH of 9.5. The solution was filtered by gravity flow, evaporated almost

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[1]All melting points are corrected; all boiling points are uncorrected.

[2]The infrared spectra were determined on a Beckman IR-5 and IR-7 with sodium chloride cells and potassium bromide pellets.

[3]The nuclear magnetic resonance spectra were determined by Melbert Peterson and Brijraj Rathore with a Varian Model A-60 high-resolution spectrometer fitted with a field-sensing stabilizer ("Super Stabilizer"). The concentration and solvent are indicated on the spectra. Tetramethylsilane was used as an internal standard.

[4]All spectra not directly recorded in the thesis are on file in the Department of Chemistry at the Oklahoma State University.

[5]The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana.

[6]Gas chromatographic analyses were performed using an Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector from Wilkens Instrument and Research, Inc.

to dryness, and placed in a drying oven at 110° overnight. Approximately 50 ml. of reagent acetone was added and the mixture was heated nearly to dryness on a hot plate. The salt was then washed with 100 ml. of reagent acetone, filtered on a Buchner funnel, dried under high vacuum for forty-five minutes and stored in a vacuum desiccator. A yield of 27.7 g. (94.2 per cent) was obtained (27).

Preparation of Sodium p-Toluate. A three-neck, round-bottom, 500 ml. flask fitted with a condenser, mechanical stirrer and addition funnel was charged with 34.0 g. (0.25 moles) of p-toluic acid (m.p. 178-179.5°) and 110 ml. of distilled water. A ten per cent solution of sodium hydroxide (10 g. in 90 ml. of distilled water) was added dropwise with stirring from the addition funnel. The solution was stirred and heated at reflux for one hour. Distillation removed most of the water, the residual traces being evaporated on a steam bath and finally by drying in an oven at 110° overnight. A yield of 34.4 g. (0.218 moles; 87.2 per cent) was obtained. Infrared analysis revealed strong absorption at 1595, 1550, 1418, 1103, 895, 887, 789, 760, and 690 cm^{-1}. The peak at 760 cm^{-1}. was assigned to para-substituted phenyl. The carbonyl absorption in the acid occurs at about 1670 cm^{-1}. However, the corresponding broad band in the spectrum of the salt is most likely at 1550 $cm.^{-1}$

Preparation of Trityl Bromide. The method for the synthesis of trityl bromide was a modification of the Organic Syntheses preparation of trityl chloride (4). A three-neck, round-bottom, 1 l. flask fitted with a mechanical stirrer, an addition funnel and a condenser with a calcium chloride drying tube, was charged with 150 g. (0.5 moles) of triphenylcarbinol and 75 ml. of dry reagent benzene. The mixture was heated until

the benzene started to reflux and a thick slurry had formed. The addition funnel was charged with 56 ml. (0.75 moles) of practical grade acetyl bromide. The acetyl bromide was slowly added to the stirred slurry. The solution was then heated at reflux for one hour after the addition of acetyl bromide was completed. The mixture (some crystals had formed) was cooled to room temperature, 125 ml. of Skelly Solvent F (b. p. 30-60°) was added, and the mixture was chilled in ice water for two hours. The light yellow, cubic crystals were filtered on a Buchner funnel, washed with 100 ml. of cold Skelly Solvent F and placed in a vacuum desiccator overnight. The trityl bromide weighed 150 g. (92.5 per cent), m. p. 153-155°.

Preparation of Trityl Pivalate (III). A three-neck, round-bottom, 1 l. flask equipped with a water condenser fitted with a calcium chloride tube, a mechanical stirrer and a nitrogen inlet tube was charged with 64.6 g. (0.20 moles) of trityl bromide, 300 ml. of reagent benzene and 27.7 g. (0.223 moles) of sodium pivalate, and the system was flushed with nitrogen. The mixture was stirred and heated at reflux under nitrogen for five hours and fifteen minutes. After cooling below reflux temperature, the warm reaction mixture was filtered on a Buchner funnel with vacuum to remove the sodium bromide and excess sodium pivalate. A yield of 26.7 g. was obtained for the combined salts. The cooled solution was filtered by gravity through a fluted filter paper to remove a small amount of insoluble material. The filtrate was concentrated on a rotary evaporator until about 70 ml. of a thick oil remained. After two days the oil had almost completely crystallized. The semi-solid was dissolved in a small amount of Skelly Solvent F (b.p. 30-60°) with heating. After standing for

about forty hours, few crystals had formed. Therefore, the volume was reduced using a rotary evaporator without heating the solution. After about six hours a considerable amount of white solid had crystallized. The solid was filtered on a Buchner funnel, washed with Skelly Solvent F and weighed; yield, 28.2 g. (40.9 per cent), m.p. 89.5-92°. Upon further reducing the volume of the filtrate, 9.4 g. (m.p. 90-93°) and 7.5 g. (m.p. 93-95°) of additional ester were obtained. An overall yield of 45.1 g. (0.131 moles) (65.5 per cent) of trityl pivalate was obtained. The infrared spectrum (Plate I) showed major absorption peaks at 1747 cm^{-1}. (carbonyl), 1140 cm^{-1}. and 702 cm^{-1}. (monosubstituted phenyl). Weaker bands at 1452 cm^{-1}. and 1368 cm^{-1}. are probably due to the tertiary butyl group (6). The nuclear magnetic resonance spectrum (Plate VI) showed peaks at 1.18 (methyl hydrogen) and 7.13 delta (aromatic hydrogen).

When the preparation was attempted using the potassium salt of pivalic acid, difficulties were encountered apparently due to a substantial solubility of the salt in the benzene. The yield of pure ester obtained was about 25 per cent.

Anal. Cald. for $C_{30}H_{24}O_2$:

C, 83.10; H, 7.20

Found: C, 83.00; H, 6.97

Preparation of Trityl p-Toluate (II). To a three-neck, round-bottom 500 ml. flask fitted with a mechanical stirrer, a nitrogen inlet tube, and a water condenser with a calcium chloride tube, was added 37.6 g. (0.238 moles) of sodium p-toluate, 64.6 g. (0.200 moles) of trityl bromide and 250 ml. of reagent benzene. The reaction mixture was heated

at reflux for two hours. After cooling just below reflux, the mixture was filtered on a Buchner funnel, and the salt was washed twice on the funnel with 50-ml. portions of hot benzene. By successively reducing the volume of the solution and filtering the crystals, three crops of impure ester were obtained (first crop--34 g., m.p. 170-185°; second crop--14 g., m.p. 160-182°; third crop--24 g., m.p. 125-135°). The total yield of crude ester was 72 g. (0.19 moles, 95 per cent). Recrystallization from 2-butanone gave pure crystals (colorless, rectangular prism crystals) which were filtered on a Buchner funnel, washed with ethyl ether, dried, weighed and stored under vacuum. The yield of pure ester obtained was 39.0 g. (0.103 moles, 52 per cent, m.p. 191-193°, Lit. 187-189° (41). The infrared spectrum (Plate II) of the ester showed major absorption bands at 1724 (carbonyl group), 1269, 1099, 966, 766, 753 and 702 cm^{-1}. (mono substituted phenyl). The peaks at 1269 cm^{-1}. and 1099 cm^{-1}. correspond to values expected for benzoate ester carbon-oxygen stretching frequency. A nuclear magnetic resonance spectrum of the ester (Plate VII) showed a singlet at 2.38 delta (methyl hydrogen), a multiplet centered at 7.21 delta and a doublet centered at 7.93 delta (both aromatic hydrogens).

Preparation of Trityl Peroxide. Trityl peroxide was prepared by the general method described by Gomberg in 1900 (20). Six grams of trityl bromide was dissolved in 50 ml. of benzene in a 125 ml. Erlenmeyer flask. To this solution was added 30 mesh zinc (about 10 g.) in small quantities until the solution had become a deep yellow brown and slightly cloudy. The mixture was then filtered under vacuum and air was bubbled through the filtrate for twenty minutes. A light yellow, fine precipitate

was filtered and washed with ethyl ether. A yield of 1.3 g. of material melting from 176-190° was obtained (m.p. 185-186°) (20). Attempted recrystallization from carbon disulfide gave crystals which, after washing with ethyl ether, melted sharply at 181°. Crystallization appeared to occur up to 190° but at 198° all the material had melted. The infrared spectrum showed major absorption bands at 1490, 1447, 1212, 1040, 978, 922, 911, 902, 771, 756, 702, and 649 cm^{-1} (Plate III). The peaks at 756 $cm.^{-1}$ and 702 $cm.^{-1}$ were assigned to monosubstitated phenyl and the band at 902 $cm.^{-1}$ could be due either to C-O stretch or O-O stretch (7).

Modification of a Bromination Method for the Quantitative Determination of Unsaturation. The bromination method described in Fritz and Hammond's "Quantitative Organic Analysis" (18) was followed with certain alterations. The method employed was as follows:

1. The sample should contain about 2 meq. of unsaturation in a volume of 25 ml. (i.e., 0.08 N) of carbon tetrachloride.

2. A calculated excess (10-15 per cent) of 0.1 N. potassium bromate-potassium bromide solution was added to a 300 ml. bromination flask from a buret.

3. The flask was evacuated using a water aspirator and 5 ml. of 6 N. sulfuric acid was added; the solution was allowed to stand for two or three minutes while the bromine was liberated.

4. A quantity (10-20 ml.) of 0.2 N. mercuric sulfate was added. Exactly 25 ml. of the sample was introduced into the flask followed by three 5-ml. portions of carbon tetrachloride to wash in all the sample and finally 20 ml. of glacial acetic acid.

5. The flask was wrapped in a black cloth and shaken for about

seven minutes.

6. Fifteen ml. of 2 N. sodium chloride and 15 ml. of 20 per cent potassium iodide were added and the contents were shaken for 30 seconds.

7. The vacuum was released and the solution was titrated with sodium thiosulfate solution to the starch endpoint.

The method indicated that benzene could be substituted for carbon tetrachloride. However, experience showed that the blank was exceedingly high when benzene was used (about 1 ml. of thiosulfate solution, instead of the 9.5 ml. expected, was required to titrate 10 ml. of the bromide-bromate solution). When the mercuric sulfate catalyst and the sodium chloride solution were omitted from the procedure, the blank was very small (about one per cent of the total titration). This slightly revised method was checked using standard solutions of 1-heptene (greater than 98 per cent pure by gas chromatography). The heptene (c.a. 0.1000 g.) was weighed out in sealed glass ampules which were preweighed before introducing the sample. The ampule was crushed in a 100 ml. volumetric flask under the solvent (both carbon tetrachloride and benzene were used) and made up to volume with the solvent. Three determinations on three aliquots of the standard solution in carbon tetrachloride using the unmodified procedure gave an average recovery (based on pure 1-heptene) of 96.5 per cent. When the modified procedure was used with aliquots from the standard solution in benzene, an average recovery of about 85 per cent was realized. However, when the reaction time was increased from seven to nine minutes with more vigorous stirring and shaking an average recovery of about 96.5 per cent was obtained on three aliquots. Also, a fresh starch solution was prepared by dissolving the starch in boiling water, cooling, and decanting the

solution from the undissolved starch. The endpoint of the titration appeared to be sharper with the fresh solution.

Pyrolysis of Trityl Pivalate (III) on the Rapid Flow System. A 300 ml. addition funnel (with a helium inlet tube) with a Teflon stopcock was used to introduce the ester onto the quartz pyrolysis column packed to a depth of 14 inches with 3/32 inch pyrex helixes. A Fisher Pyrometer Controller of the thermo-couple type was used to control and record the temperature. The furnace was an Electric Multiple Unit Furnace made by Hevi-Duty Electric Co. The trap system consisted of an ice-cooled receiver flask (500 ml., round-bottom flask with a B-10 neck), a dry ice-acetone trap, a pre-weighed U-tube filled with Ascarite, and two liquid nitrogen traps.

Exactly 23.719 g. (0.0689 moles) of trityl pivalate (III) was dissolved in 100 ml. of reagent benzene and washed into the addition funnel with 50 ml. of additional benzene. The pyrolysis system was flushed with helium gas for two hours before the oven heater was started and for two hours after the temperature reached 425°. The ester was then pyrolyzed at a drop rate of 25-30 drops per minute. The helium flow rate was maintained at about 20 ml. per minute. Gas samples were collected by displacement of salt water after three hours. An infrared spectrum of the gas indicated that any volatile products which might have been formed remained in the traps. After the pyrolysis was completed (total time, 5.5 hours), 50 ml. of benzene was dropped through the column at a rate of about 60 drops a minute. The ice water was removed from around the receiver flask, and the system was allowed to stand for one-half hour at 425° under the same helium pressure. The traps were then closed and the

Ascarite U-tube was reweighed after flushing it briefly with air. The column, after cooling, was washed with five 50-ml. portions of hot benzene to remove products adhered to the packing. The infrared spectrum of the pyrolysate showed no carbonyl absorption and appeared to resemble only triphenylmethane (Plate IV). Infrared analysis of the gaseous contents of the dry ice-acetone and first liquid nitrogen traps showed the presence of benzene and isobutylene with absorption bands at 3100, 2975, 2750, 1960, 1800, 1465, 1398, 1383, 1282, 1053, 1038, 988, 910, 890, 875, 690, 675, and 665 $cm.^{-1}$ The spectra were compared to spectra of the known pure compounds and were unequivocally substantiated.

An attempt was made to trap the isobutylene as its dibromide by gradually warming the traps and directing the expanding gases through two bromine-bromine water traps and a sodium thiosulfate trap (the last trap was to destroy any bromine vapors which would otherwise escape into the air). After the traps reached room temperature, the contents were flushed with helium for one-half hour into the bromine trap system. The contents of the bromine traps were then poured into about 500 ml. of a sodium thiosulfate solution to destroy the excess bromine. The sulfur which formed was filtered and washed with ethyl ether. The filtrate was extracted with three 50-ml. portions of ethyl ether. After concentrating the ether extracts, additional sulfur precipitated which was filtered and washed with a small amount of cold ether. The filtrate was concentrated to a heavy oil which weighed 2.5845 g. A small sample was removed for nuclear magnetic resonance studies which showed isobutylene dibromide and an impurity (peaks at 7.32, 3.92, 3.83, 1.98, 1.86 delta). A nuclear magnetic resonance spectrum of known isobutylene dibromide was also taken (peaks at 3.83 and 1.87 delta).

The pyrolysate was washed into a 500 ml. volumetric flask and diluted to volume with reagent benzene. A 100 ml. aliquot was removed for analysis by gas chromatography. The remainder was concentrated and chromatographed on acid-washed alumina (Merck reagent grade). The products were eluted from the column using 100 ml. of Skelly Solvent B (b.p. 60-90°); 450 ml. of cyclohexane; 800 ml. of benzene; 350 ml. of 85:15 benzene: ethyl ether; 400 ml. of 60:40 benzene: ethyl ether; 150 ml. of 20:80 benzene: ethyl ether; 100 ml. ethyl ether; and 250 ml. methanol. Four components were identified in the effluent by gas chromatography using a column composed of 20 per cent SE-30 on acid-washed chromosorb W (6 ft.) with the hydrogen flame detection unit. Biphenyl (1 minute 20 seconds), benzophenone (2 minutes 5 seconds), triphenylmethane (4 minutes 35 seconds) and triphenylcarbinol (6 minutes 20 seconds) were identified by gas chromatography at 288°. A yellow-colored material was also eluted but was not identified. The triphenylmethane eluted was combined, dried under high vacuum and weighed (m.p. 91-92.5°) (Plate IV).

The only product detected in the sample taken for gas chromatographic study was triphenylmethane. This was not surprising in view of the small quantities of the other components found in the effluent from the chromatography on alumina. At 34° and 100° isobutylene was identified using a 10% di-n-butylphthalate on fluoropak 90 column (6 ft.). At a carrier gas flow rate of 26 ml. per minute the retention times were 1 minute 50 seconds and 1 minute 5 seconds at the respective temperatures. Isobutylene was also detected in the benzene solution found in the dry ice-acetone trap.

The isobutylene found in both the pyrolysate and in the benzene

solution in the first dry ice-acetone trap was determined by the bromination method described by Fritz and Hammond (18) with certain modifications. The exact procedure has been described in a separate experiment. A solution prepared by bubbling known isobutylene through benzene was also analyzed by this method. The yield of isobutylene was calculated directly from the data obtained using this method and indirectly by comparison of areas on the gas chromatograph using a 10% di-n-butylphthalate column. The standard solution described above was used as a reference for comparison in the gas chromatographic analysis. The two methods gave nearly identical results (0.0222 moles isobutylene via gas chromatography, 0.0250 moles via direct bromination method). Including the isobutylene isolated as the di-bromide, the total yield was 0.037 moles of isobutylene. This value was probably low in view of the time elapsed before the determinations were made and the low results (85 per cent recovery) obtained on preliminary determinations with standard solutions of known concentrations of both 1-octene and 1-heptene.

In summary, the following compounds were identified and corresponding yields obtained (See Table I).

TABLE I

RESULTS FROM FIRST TRITYL PIVALATE (III) PYROLYSIS

Compound	Wt. in g.	Mole	Per Cent Based On Starting Ester (0.0689 Moles)
Carbon Dioxide	2.6949	0.0602	87.4
Triphenylmethene	15.3156	0.0627	91
Isobutylene		0.037	54
Benzophenone	trace		trace
Biphenyl	trace		trace
Triphenylcarbinol	trace		trace

In a previous pyrolysis of the ester at 350°, only a small amount of carbon dioxide (about 20 per cent) was obtained and an infrared spectrum of the pyrolysate indicated the presence of a large amount of unpyrolyzed trityl pivalate. However, isobutylene was found in the traps.

The ester was pyrolyzed a second time at 425° in order to obtain a more accurate determination of isobutylene and to check the analysis of the other products. The apparatus was identical to that used previously except for the trap system. The latter was composed of the ice-cooled receiver flask, a gas scrubber (with a fritted tip) filled with 200 ml. of cold benzene (maintained at about 10°), a dry ice-acetone trap, an Ascarite trap and a liquid nitrogen trap. When the pyrolysis was completed, the dry ice-acetone and the liquid nitrogen traps were warmed to room temperature and purged with helium through another gas scrubber containing 200 ml. of cold benzene. The benzene solutions from the two gas scrubbers were combined and diluted to 500 ml. in a volumetric flask. The pyrolysate from the receiver flask was also diluted to 500 ml. in a volumetric flask. Triplicate determinations were made on each of the two solutions. Duplicate blanks were run on each sample also. Blanks for the pyrolysate were prepared by evaporating a 10 ml. aliquot (same as used in the determination) to dryness on a rotary evaporator and drying for 10 minutes under high vacuum. The solid was then redissolved in 40 ml. of reagent benzene. A 40 ml. quantity of reagent benzene was used as the blank for the benzene solution from the scrubbers. The results obtained for the pyrolysate were 1.35, 1.37 and 1.36 meq. of unsaturation in 10 ml. samples. The determinations on the trap solutions gave 1.09, 1.07 and 1.09 meq. in 20 ml. samples.

The pyrolysate was chromatographed on alumina and studied by gas

chromatography as before. The results are summarized in Table II.

TABLE II

RESULTS FROM SECOND TRITYL PIVALATE (III) PYROLYSIS

Compound	Wt. in g.	Moles	Percent yield Based on Starting Ester (0.0555 Moles)
Isobutylene		0.0476	86
Carbon Dioxide	1.9639	0.0446	80.4
Triphenylmethane	12.484	0.0511	92
Biphenyl	trace		trace
Benzophenone	trace		trace
Triphenylcarbinol	.9114	.0035	6

Static Pyrolysis of Trityl p-Toluate (II). The pyrolysis apparatus consisted of a two-neck, round-bottom, 50 ml. flask fitted with a helium inlet tube and a water condenser. The trap system was composed of two dry ice traps, an Ascarite scrubber, a liquid nitrogen trap, a blank and a palladium chloride scrubber (about 0.010g. in 20 ml. of water). A molten bath of sodium nitrate and potassium nitrate (ratio 65:80) was used as the heat traveler medium for pyrolysis of the ester.

Exactly 7.8095 g. (0.02063 moles) of trityl p-toluate (II) was weighed into the pyrolysis flask. The traps were pre-weighed and the system was purged with helium for 30 minutes while the salt bath was being heated. When the bath temperature had reached 320°, the pyrolysis flask was slowly immersed (helium flow rate--25 ml. per minute). The temperature, after dropping to 290°, rose to 335° within 15 minutes and to 343° within 30 minutes (it was held at this temperature for an hour). The pyrolysis flask and the two dry ice traps were allowed to come to

room temperature under helium at the same pressure. An infrared spectrum of the contents of the liquid nitrogen trap showed it to be empty. The Ascarite scrubber absorbed 0.9645 g. (0.00147 moles) of carbon dioxide and the palladium chloride suspension indicated a trace of carbon monoxide. The first trap contained 0.0350 g. of toluene and a trace of benzene (identified on a 20% Apiezon L column). The pyrolysate was dissolved in ethyl ether and filtered to remove the insoluble material (ether soluble fraction called fraction 1). The insoluble matter was treated successively with benzene (fraction 2) and acetone (fraction 3). A small amount of material remained undissolved (fraction 4). Infrared spectra of all fractions were obtained. Fraction 1 appeared to contain triphenylmethane, p-toluic acid and an anhydride (probably p-toluic anhydride as the spectrum was quite similar to that of benzoic anhydride). Fractions 2 and 3 appeared to contain p-toluic anhydride and other materials (possibly polymeric). These two dark brown fractions were combined as their spectra were identical and they had about the same melting range (135° to 200°). The spectrum of fraction 4 contained only a few broad weak bands.

Fraction 1 was diluted to 500 ml. with ether. The acid and anhydride were extracted from a 200 ml. aliquot with exactly 70 ml. of 0.1181 N sodium hydroxide solution in three portions and two 20-ml. portions of water. The basic extract was back-titrated with 0.1000 N hydrochloric acid using a Beckman Model 72 pH meter. The equivalence point was determined from the titration curve. A yield of 77.5 per cent was calculated by this method. By precipitating the acid, filtering, drying and weighing, a yield of 75.5 per cent was calculated. An attempt to extract only the acid from another 200 ml. aliquot using 7 per cent sodium

bicarbonate solution failed as the anhydride was removed also. The two extracted solutions of fraction 1 were combined and a 20 ml. aliquot (0.1 of the extracted portion or 0.08 of fraction 1) was removed for gas chromatographic studies. The remainder was chromatographed on alumina (Merck Reagent Grade) using 1.3 l. Skelly Solvent F (b.p. 30-60°), 300 ml. cyclohexane, 400 ml. benzene, 1.1 l. ethyl ether, 300 ml. ethanol, 100 ml. methanol and 100 ml. carbon tetrachloride. The cuts (about 70 ml. each) were followed by gas chromatography on a 10% Silicone Rubber column. The compounds detected were triphenylmethane, the unknown 2, 9-phenylfluorene and benzophenone. 9-Phenylfluorene was identified by melting point (m.p. 144-147°, Lit. 148° (36) and by comparison of the infrared spectrum with that of an authentic sample. The two spectra were superimposable (see Plate V).

The cuts containing triphenylmethane and 9-phenylfluorene were combined, dried and weighed. The aliquot set aside for gas chromatographic studies was transferred to a 10 ml. volumetric flask. After adding 0.0307 g. of benzil (internal standard), the amount of benzophenone, 9-phenylfluorene, and unknown 2 were determined by comparison with three synthetic standard solutions by the internal standard method. A summary of the results obtained is shown in Table III.

Further attempts were made to purify and characterize the material in fractions 2 and 3. Precipitation from acetone upon the addition of ethyl ether was unsuccessful. The material was completely soluble in base, liberating carbon dioxide from sodium bicarbonate solution. The base hydrolyzed all anhydride present. A nuclear magnetic resonance spectrum of the material in acetone showed peaks at 3.85, 6.88, and 7.55 delta in a ratio of 3:2:1, respectively. A small peak was observed at 2.8 delta. A

spectrum of the material in dilute (about 0.4 N) sodium hydroxide solution was compared to that of a similar solution of p-toluic acid and were found to be markedly different. An ultra violet spectrum of the material in absolute ethanol showed major absorption at about 320 and 238 millimicrons with shoulders at 315 and 345 millimicrons. A peak at 236 millimicrons has been reported for p-toluic acid in 99.5 per cent water and 0.5 per cent ethanol (29).

TABLE III

RESULTS FROM STATIC PYROLYSIS OF TRITYL P-TOLUATE UNDER HELIUM

Compound	Wt. in g.	Moles	Per Cent Yield Based On Starting Ester (0.02063 Moles)
Unknown 2	trace		trace
Benzophenone	0.189	0.00104	5.04
Triphenylmethane	3.6598	0.01498	72.6
9-Phenylfluorene	0.65	0.0027	13
p-Toluic Acid and Anhydride (reported as acid)	2.1769	0.01599	77.5
Toluene	0.0350	0.00038	1.8
Benzene	trace		
Carbon Dioxide	0.0645	0.00147	7.1
Carbon Monoxide	trace		
Fractions 2 and 3	0.6402		
Fraction 4	0.0693		

A second static pyrolysis was run in much the same manner except that oxygen was bubbled through the pyrolysate during the pyrolysis. The temperature was maintained at 340° for 35 minutes after a 25-minute

preheating period. The ether soluble portion (fraction 1) was analyzed as before. The insoluble material was treated with acetone (fraction 2) and filtered (completely insoluble material, fraction 3). The infrared and ultraviolet spectra of fractions 2 and 3 were very similar to those obtained for the corresponding fractions in the previous pyrolysis. Fraction 2 was soluble in base, liberating carbon dioxide from sodium bicarbonate solution. An infrared spectrum of material from the condenser was nearly superimposable on the spectrum of pure phenol except for a few peaks corresponding to p-toluic acid. An increased yield of benzene was obtained and a new unknown (unknown 3) was detected in several of the cuts from the chromatography on alumina. An infrared spectrum of a cut containing the unknown and benzophenone showed a carbonyl band at 1740 $cm.^{-1}$ as well as the carbonyl for benzophenone at 1660 $cm.^{-1}$ A small amount of triphenylcarbinol and an appreciable amount of benzophenone were determined by the internal standard method on the hydrogen flame gas chromatograph. The data obtained is summarized in Table IV.

A typical chromatogram of this pyrolysate on the 10 per cent Silicone Rubber on Chromosorb W column (8 ft.) at a carrier gas flow rate of 28 ml. per minute showed the following retention times for a column temperature of 259° (See Table V).

TABLE IV

RESULTS FROM STATIC PYROLYSIS OF TRITYL
P-TOLUATE IN PRESENCE OF OXYGEN

Compound	Wt. in g.	Moles	Per Cent Yield Based On Starting Ester (0.02153 Moles)
Carbon Dioxide	0.0367	0.000834	3.9
Carbon Monoxide	trace		
Benzene	0.0228	0.00029	1.3
Toluene	0.0506	0.00055	2.6
p-Toluic Acid and Anhydride (as acid)	2.7806	0.02042	95
Phenol	small amt.		
Biphenyl	trace		
Unknown 1	trace		
Benzophenone	0.3805	0.00209	9.7
Unknown 3	trace		
Triphenylmethane	3.1444	0.1289	60
Triphenylcarbinol	0.0510	0.000196	0.9
Fraction 2	0.7394		
Fraction 3	0.2718		

TABLE V

RETENTION TIMES FOR PYROLYSIS PRODUCTS

Compound	Retention Time
Biphenyl	1 minute 5 seconds
Unknown 1	2 minutes
Benzophenone	2 minutes 50 seconds
Unknown 3	4 minutes
Triphenylmethane	6 minutes 35 seconds
Triphenylcarbinol	9 minutes 20 seconds

Pyrolysis of Trityl p-Toluate (II) on the Rapid Flow System. The apparatus employed was the same as described in the previous experiment

with the following exceptions. The pyrolysis column was packed to a depth of 11 inches. The trap system was composed of the ice-cooled receiver flask, a dry ice trap, an Ascarite scrubber, a blank trap and a palladium chloride scrubber (0.010 g. palladium chloride suspended in 20 ml. of water) (1).

Exactly 10.6168 g. (0.02805 moles) of trityl p-toluate (II) was dissolved in 200 ml. of reagent benzene and the solution was washed into the 300 ml. addition funnel with 20 ml. of additional benzene. The helium flow rate was maintained at about 25 ml. per minute. The solution was dropped on the column (temperature 425°) at a rate of 30 to 40 drops per minute. When the pyrolysis was completed, 25 ml. of benzene was dropped through the column. The column was allowed to cool to room temperature and was then washed with 200 ml. of hot benzene. A considerable amount of charring was observed about 1 inch from the top and 2 inches from the bottom of the column packing. A small amount of carbon monoxide was detected in the palladium chloride trap and 0.3233 g. (0.00735 moles) of carbon dioxide was absorbed by the Ascarite scrubber. In a previous pyrolysis, infrared analysis of gas samples indicated carbon dioxide and traces of carbon monoxide as the only gases produced (carbon dioxide 2350 $cm.^{-1}$ and carbon monoxide 2150 $cm.^{-1}$). An infrared spectrum of the pyrolysate showed a carbonyl at 1670 $cm.^{-1}$ (same as p-toluic acid) and the peaks characteristic of triphenylmethane (Plate IV). The pyrolysate was made up to 500 ml. with benzene in a volumetric flask. A 200 ml. aliquot was chromatographed on alumina (Merck Reagent Grade) using 700 ml. Skelly Solvent F (b.p. 30-60°); 50 ml. of 1:1 Skelly F: cyclohexane; 50 ml. 1:3 Skelly F: cyclohexane; 300 ml. cyclohexane; 50 ml. 1:1 cyclohexane; benzene; 700 ml. benzene; 50 ml. each of 1:3, 1:1, and

1:3 benzene: ethyl ether; 700 ml. ethyl ether; 50 ml. of 1:1 ethyl ether: methanol and 400 ml. methanol. The cuts (about 75 ml. each) containing triphenylmethane were combined, dried and weighed.

Another 200 ml. aliquot of the pyrolysate solution was extracted with two 40-ml. portions of a solution of sodium bicarbonate (3 g. in 80 ml. of water) and 20 ml. of water. An infrared spectrum of the organic layer indicated the acid had been removed. The basic extract was acidified carefully with concentrated hydrochloric acid. The precipitate, after standing overnight, was filtered on a Buchner funnel, washed with 20 ml. of dilute acid and 5 ml. of water. After drying on the funnel for two hours and in a desiccator for several days, the acid (m.p. 179-80°, Lit. 180° (17).) was weighed. In a previous pyrolysis, nearly identical results were obtained via a back-titration with standard hydrochloric acid on an extract of the acid made with a known quantity of standard base (sodium hydroxide solution), and by the method described above.

The organic solution above (with the acid removed) was reduced in volume and placed in a 50 ml. volumetric flask. Exactly 0.1924 g. of benzil was added as a standard, and the solution was diluted to volume with ether. An unknown and triphenyl carbinol were estimated quantitatively by gas chromatography on the hydrogen flame unit using the internal standard method (30) and three synthetic mixtures containing benzil, triphenylcarbinol, benzophenone, triphenylmethane, and 9-phenylfluorene. Qualitative analysis of the pyrolysate and the effluent from alumina chromatography by infrared analysis and gas chromatography indicated the presence of traces of biphenyl and benzophenone also.

A summary of the results is shown in Table VI.

TABLE VI

RESULTS FROM RAPID FLOW PYROLYSIS OF TRITYL P-TOLUATE (II)

Compound	Wt. in g.	Moles	Per Cent Yield Based on Starting Ester(0.02805 Moles)
Carbon Dioxide	0.3233	0.00735	26
Carbon Monoxide	trace		trace
p-Toluic Acid	1.8140	0.01332	48
Biphenyl	trace		trace
Benzophenone	trace		trace
Triphenylmethane	5.3855	0.02207	79
Triphenylcarbinol	0.305	0.00117	4
Unknown 1	0.146		

A previous pyrolysis run at a temperature of 375° was incomplete as about 25 per cent of the ester II was recovered. Considerable charring occurred also. The pyrolysate was taken almost to dryness and dissolved in ethyl ether (the ester is sparingly soluble and dissolved to a negligible extent). The pyrolysate was analyzed as above. However, 0.248 g. of material obtained from the chromatography on alumina (cuts 36-39) was identified as trityl peroxide by infrared analysis (see Plate III), melting point, and mixed melting point with a sample prepared by a known method (20).

Photolysis of Trityl p-Toluate (II). A slowly stirred solution of trityl p-toluate (II) (4.9803 g., 0.01316 moles) in 40 ml. of benzene was photolyzed in a quartz, round-bottom 100 ml. flask with a 140 watt, 3.9 amp. Hanovia ultraviolet lamp for a period of 71 hours under a nitrogen atmosphere at a temperature of about 60° (heat was supplied by the lamp

only). An infrared spectrum of the photolysate indicated the presence of a small amount of p-toluic acid (peak at 1670 $cm.^{-1}$) and a large amount of ester II. Upon extraction of the photolysate solution with 5 per cent sodium bicarbonate solution, followed by careful acidification of the extract with concentrated hydrochloric acid, a precipitate was obtained. The sample dried in a desiccator weighed 0.1657 g., m.p. 178-180°, Lit. 180° (17). Extraction of pure ester by the same procedure gave no acid.

The organic layer was studied by gas chromatography on the hydrogen flame unit and by infrared spectroscopy. No acid carbonyl appeared in the infrared spectrum. The chromatogram indicated the presence of triphenylmethane, benzophenone, triphenylcarbinol and an unknown (corresponding to unknown 1 in previous experiments). Injections of pure ester II on the gas chromatograph gave a large peak corresponding to triphenylmethane and small peaks corresponding to the other products. Therefore, an aliquot of 50 ml. of the total solution (100 ml.) was evaporated almost to dryness. The photolysate was stirred at reflux with 40 ml. of water containing 15 g. of sodium hydroxide for 10 hours. Ethyl ether was added and an infrared spectrum of the organic layer showed the presence of only triphenylcarbinol (no ester present). The two layers were separated and the organic portion was transferred to a 25 ml. volumetric flask for further studies by gas chromatography.

Qualitative studies on a 10% silicone rubber on Chromosorb W (8 ft.) showed the presence of small amounts of the unknown 1, benzophenone and triphenylmethane. A large amount of triphenylcarbinol from the hydrolysis of the ester was present. The first three compounds above were determined quantitatively after adding 0.0700 g. of benzil as the internal standard by

comparison with three synthetic standards.

The data obtained is summarized in Table VII.

TABLE VII

RESULTS FROM PHOTOLYSIS OF TRITYL P-TOLUATE (II) UNDER NITROGEN

Compound	Wt. in g.	Moles	Per Cent Yield Based On Starting Ester (0.01316 Moles)
Unknown 1	0.018		
Benzophenone	0.037	0.00020	1.6
Triphenylmethane	0.029	0.00012	0.9
Triphenylcarbinol	Not determined (residual ester hydrolyzed to acid and triphenylcarbinol.)		
p-Toluic Acid	0.1657	0.00122	9.3

Another run was made in an identical manner except a slow stream of oxygen was bubbled through the ester solution throughout the photolysis (73 hours). The temperature was maintained at about 70° by the heat from the lamp. Increased amounts of p-toluic acid, benzophenone and triphenyl carbinol were observed. Exactly 0.1744 g. of benzil was added to the hydrolyzed photolysate for chromatographic studies. The results are summarized in Table VIII.

TABLE VIII

RESULTS FROM PHOTOLYSIS OF TRITYL P-TOLUATE (II) IN PRESENCE OF OXYGEN

Compound	Wt. in g.	Moles	Per Cent Yield Based On Starting Ester (0.01419 Moles
Unknown 1	0.0127		
Benzophenone	0.146	0.000802	5.7
Triphenylmethane	0.0185	0.000076	0.5
Triphenylcarbinol	Not determined, but an appreciable amount is present based on gas chromatogram of photolysate before hydrolysis.		
p-Toluic Acid	1.0548	0.007748	55

A solution of 4.9549 g. of trityl p-toluate (II) in 40 ml. of benzene was heated at 65° in the dark for 72 hours under a nitrogen atmosphere. The solution was then extracted with 25 ml. of 5 per cent sodium bicarbonate and 20 ml. of water. Upon careful acidification with concentrated hydrochloric acid, no precipitate formed in the extract. A gas chromatogram of the solution was identical to that of the pure ester.

Photolysis of Triphenylmethane in Presence of Oxygen. A solution containing 1.407. g. (0.00576 moles) of triphenylmethane in 25 ml. of reagent benzene was photolyzed for 61 hours with slow stirring and a slow stream of oxygen bubbling through the solution at reflux. The yellow photoysate was studied by gas chromatography on the 10% silicone rubber on Chromosorb W column (8 ft.). Biphenyl, benzophenone, triphenylcarbinol and starting material were all identified with the first three compounds present in trace quantities (less than 1 per cent).

Plate I

Trityl Pivalate (III), KBr Pellet

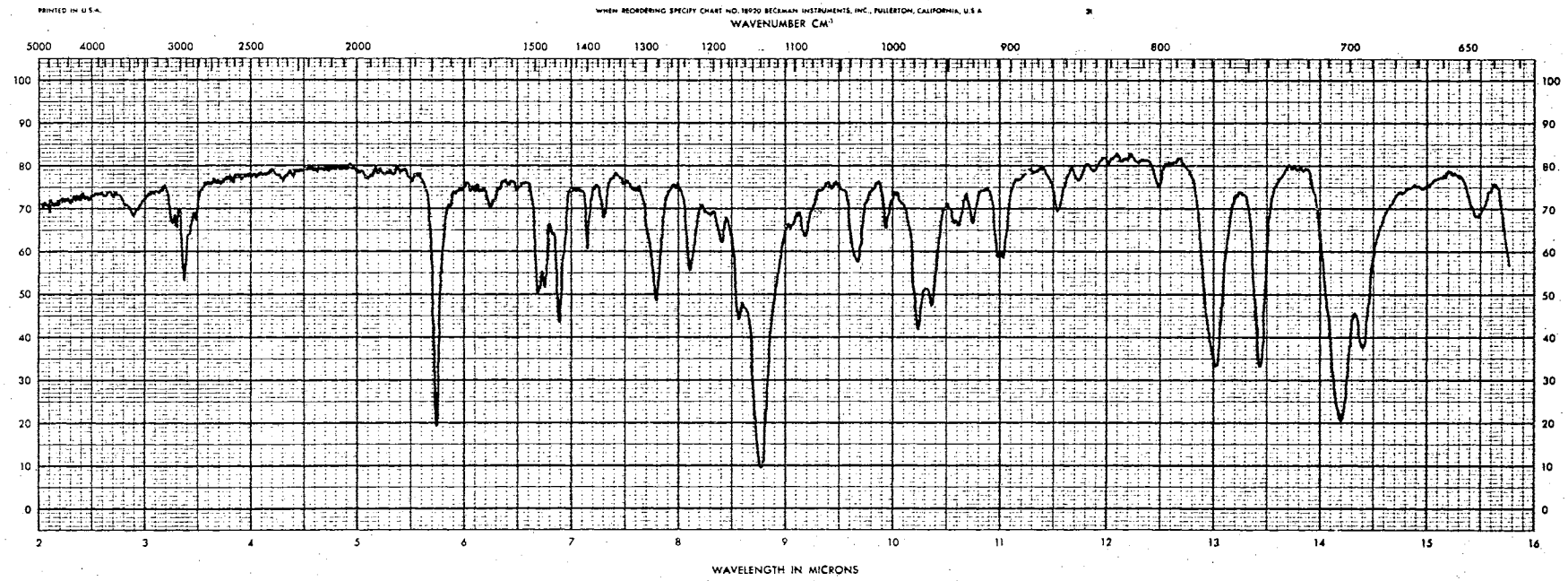


Plate II

Ttâtyl p-Toluate (II), KBr Pellet

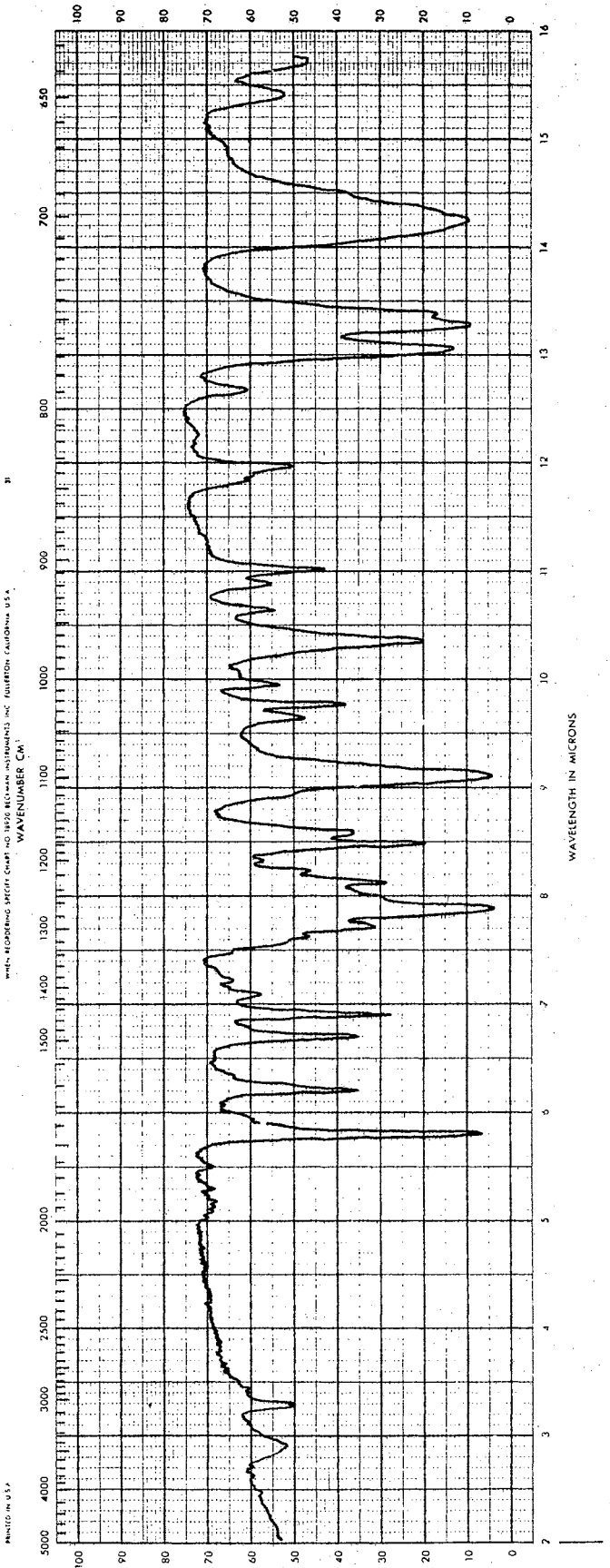


Plate III

Trityl Peroxide, KBr Pellet

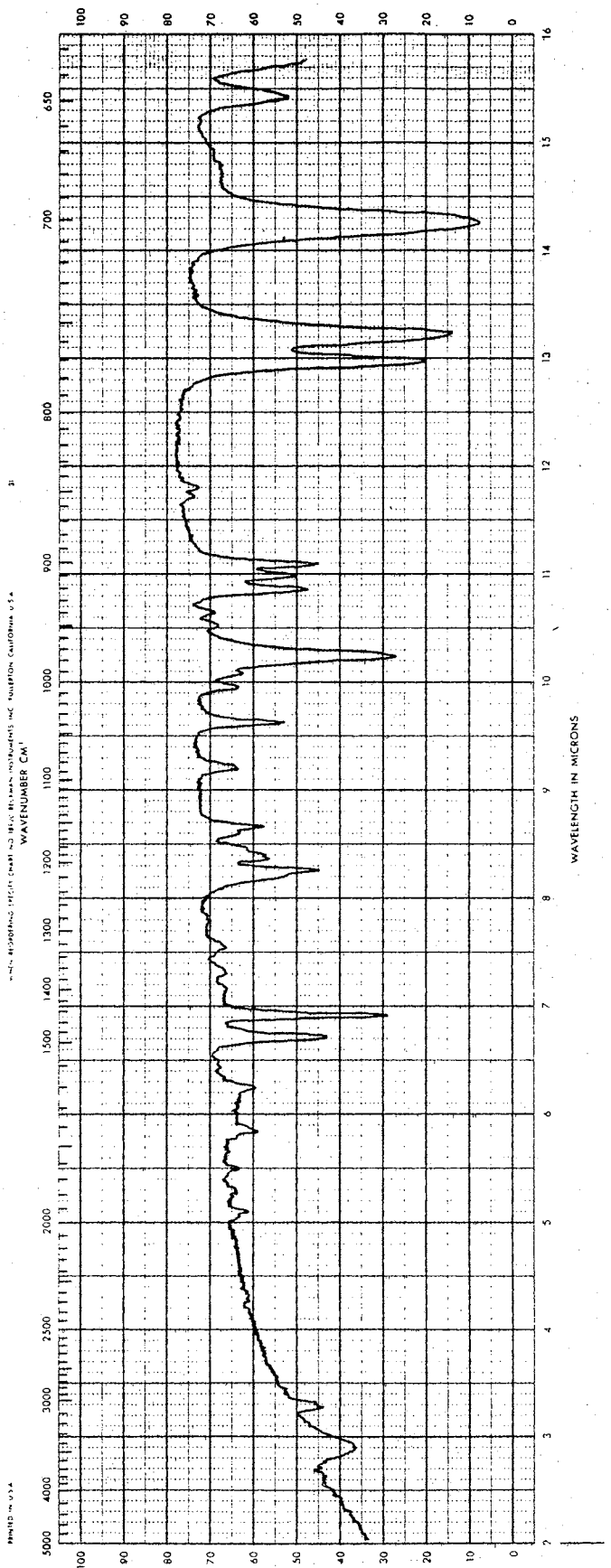


Plate IV

Triphenylmethane, KBr Pellet

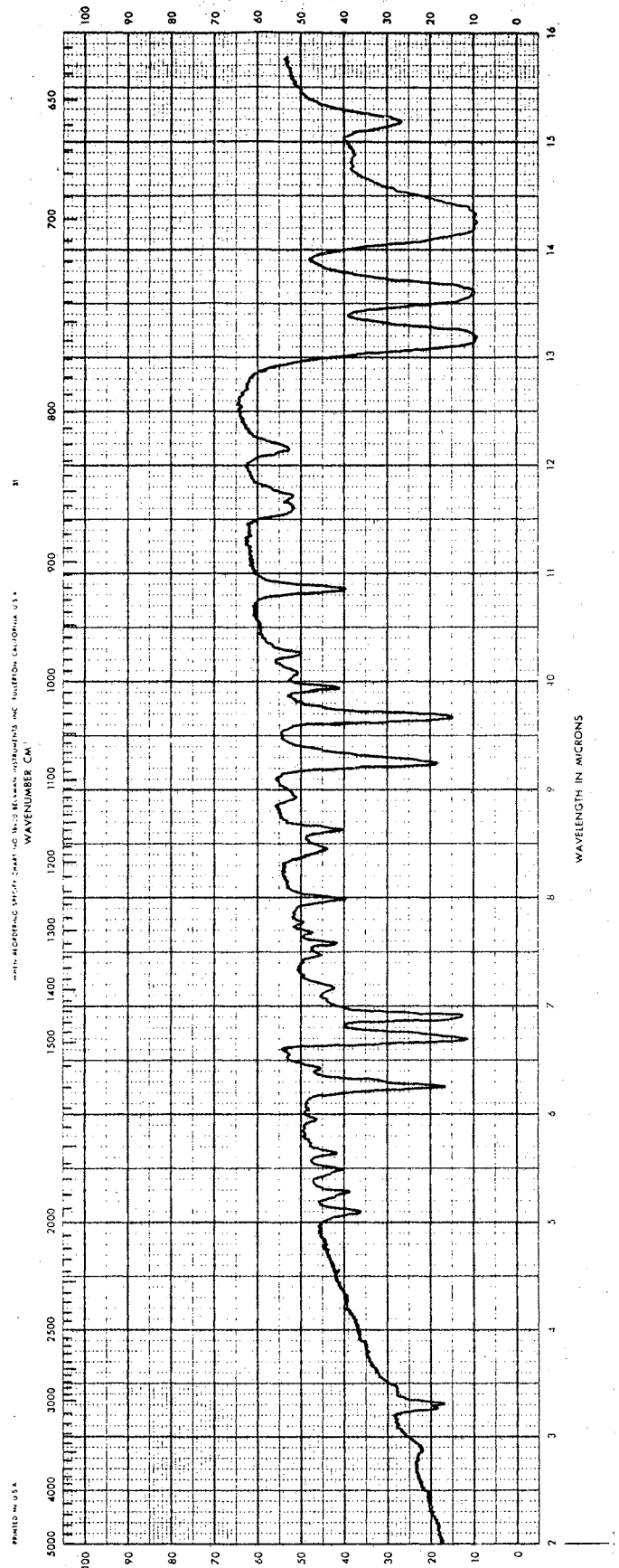


Plate V

9-Phenylfluorene, KBr Pellet

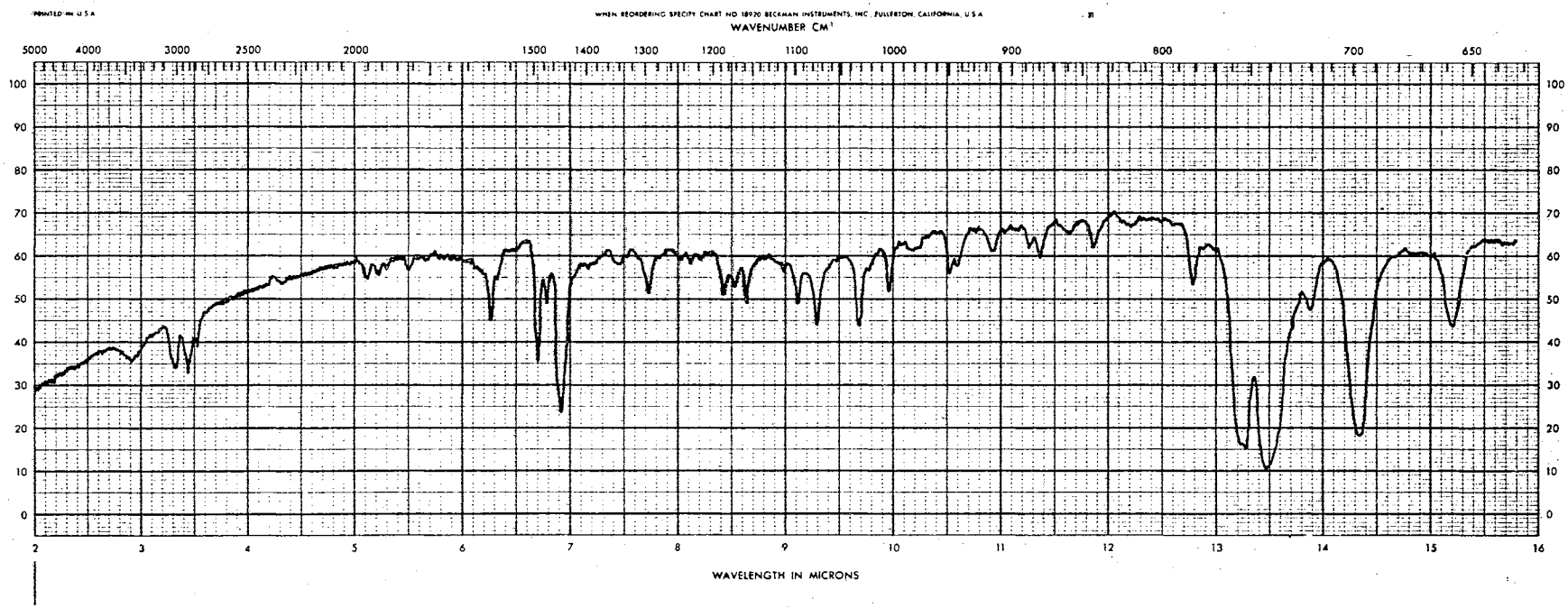


Plate VI

Solvent.....5% in CCl_4 S.W. ...500 cps Trityl Pivalate (III)
F.B. .....1 cps S.O. ...000 cps
R.F. Field..0.2 mG S.A. ...6.3
S.T. .....250 sec I.A. ...off

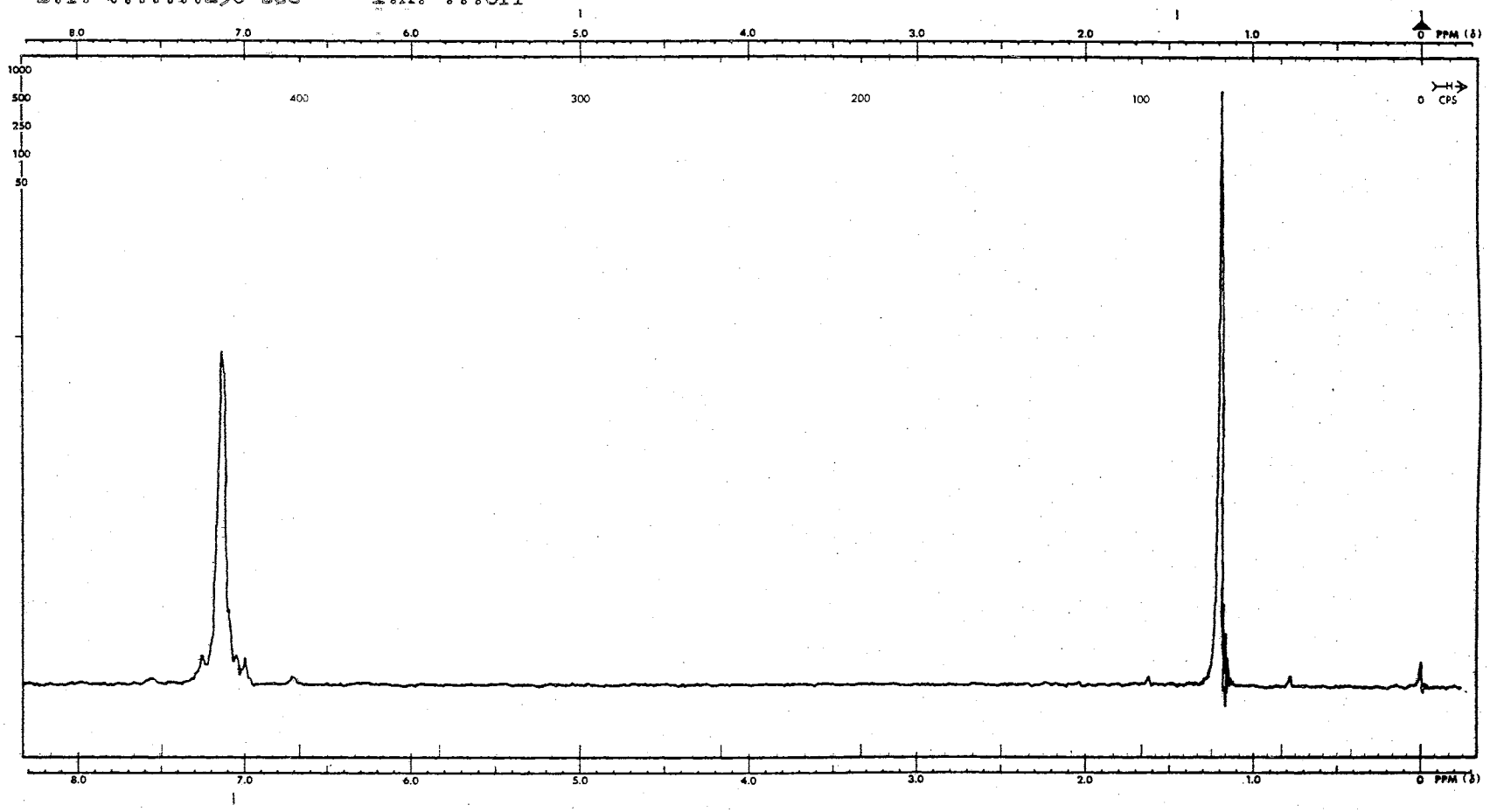
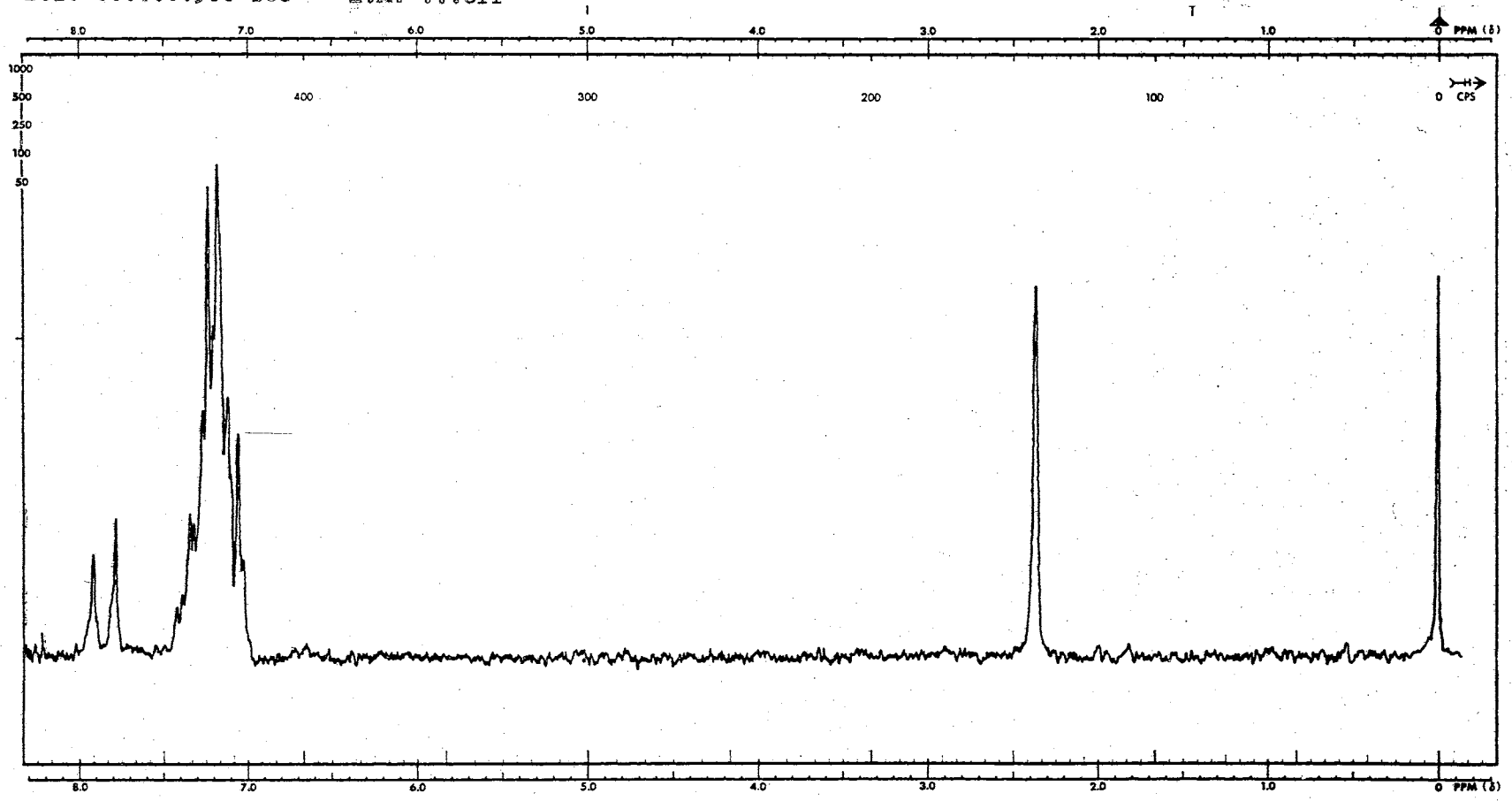


Plate VII

Solvent.....Sat. CCl_4 S.W. ...500 cps
F.B. .....0.4 cps S.O. ...000 cps
R.F. Field..0.2 mG S.A. ...32
S.T. .....500 sec I.A. ...off

Trityl p-Toluate (II)



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